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PAH Biodegradation, Turnover, and Ambient Concentration in Surface Sediments of Coaster's Harbor and Narragansett Bay

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14. ABSTRACT
PAH concentrations in the Coaster's Harbor site were generally low when compared with surface sediment data from other estuaries. The highest PAH concentration in the NRL survey was found at station 2, which was in a ship anchorage, whereas the station closest to the firefighting training area (11) had among the lowest concentrations found. Low naphthalene concentrations in all samples suggest that the PAH source is not likely to be from a fresh spill or groundwater intrusion of dilute unweathered product. Determining the mass of PAH in sediments at the Coaster's Harbor site would be difficult given the large amount of benthos covered by rock or confluent with eelgrass. PAH biodegradation rates were rapid given the low ambient concentrations, suggesting that current surface water inputs of P AH would likely be metabolized in less than 100 days.

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CONTENTS

PAH BIODEGRADATION, TURNOVER AND AMBIENT CONCENTRATION IN SURFACE SEDIMENTS OF COASTER'S HARBOR AND NARRAGANSETT BAY

EXECUTIVE SUMMARY

PAH Concentration

Total PAH concentrations in the nine samples from Coaster's Harbor and in the six samples from Narragansett Bay ranged from below 0.1 to 3.2 ppm for all samples (Tables 1 and 2). The Tetratech sampling of the same site two weeks earlier found PAH values in this same range for 11 of their 13 samples. Most samples had naphthalene concentrations that were low or near detect suggesting that the PAH composition is not likely to be from a fresh spill (Table 2). Two samples (9.5 and 10.2 ppm total PAH) were higher than this range found with the NRL samples though it is not clear if these are statistically different. The range of 0.1 to 10.2 ppm total PAH for all 28 samples in the combined survey is generally low among the estuaries that have been seasonally sampled by NRL (Table 3; Boyd et al. 1999, Montgomery et al. 2002, Pohlman et al. 2002).

PAH Biodegradation

PAH biodegradation was measured using the rate of bacterial mineralization of the ^{14}C-radiolabelled compounds, naphthalene, phenanthrene and fluoranthene to CO_2 in 24 h incubations (Boyd et al. 1999). ^{14}C-catechol mineralization was also measured as an indication of aromatic organic matter degradation. These sentinel compounds were chosen because they represent a large portion (20-30%) of the total PAH compounds commonly found in estuarine sediments. In the NRL and Tetratech samplings in July, the three PAH compounds comprised 27% of the total measured PAHs from all samples. Mineralization rates ranged from non-detect (below 1.0×10^{-7} $\mu g\ g^{-1}\ d^{-1}$) to 4.8×10^{-3} $\mu g\ g^{-1}\ d^{-1}$ (Table 4). These degradation rates are mid range for the estuarine sediments studied to date (Charleston Harbor, Delaware Bay, Chesapeake Bay, San Francisco Bay, and San Diego Bay) and are common to sediment that do not chronically receive high input of PAH (Katz 1998, Montgomery et al. 2002). Sediments that are subject to elevated flux of PAH from surface waters or shore side sources have mineralization rates up to four orders of magnitude higher than the highest measured in this study of Narragansett Bay sediment.

PAH Turnover

The turnover of a compound is determined by dividing the ambient concentration by the mineralization rate. It is a measure of the length of time that the contaminant would take to be completely removed from the sediment by bacteria if the mineralization rate did not change and there were no new inputs of PAH to the sediment. Based on our data from the other estuaries, areas that have high ambient total PAH concentrations (>10 ppm) and rapid turnover times (< 100 days) are likely to be receiving PAH inputs that are high enough to select for a PAH-degrading bacterial assemblage. No ambient concentrations of naphthalene were measured so the turnover time is not a meaningful measure for this compound (Table 5). All but four of the stations had rapid turnover times (less than 100 days), for one of both of the other PAH compounds, relative to most sediment samples taken during our ecosystem surveys. It should be cautioned that both

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the PAH concentration and mineralization measurements are at the lower end of the analytical detection. Even though many of the turnover times are rapid, the ambient PAH concentration is low so this data would not support the conceptual model that there are current sources of PAH to the surface sediment that are statistically different than those found throughout the watershed.

Bacterial Production

Bacterial metabolism, also called bacterial production, was measured from the rate of incorporation of ^{3}H-leucine into bacterial proteins (Kirchman et al. 1985, Smith and Azam 1992, Kirchman 1993). Bacterial production can be inhibited by elevated concentrations of PAH in estuarine sediments. In this study, we found production ranging from 4.1 to 34.2 μg C kg^{-1} d^{-1} but could not demonstrate a relationship with ambient PAH concentration (Table 6) because the PAH concentrations were too low. This is not surprisingly as an inhibitory effect on metabolism is typically not found below 20 ppm of total PAH when comparing these values in other coastal ecosystems.

Conclusions

PAH concentrations in the Coaster's Harbor site were generally low when compared with surface sediment data from other estuaries. The highest PAH concentration in the NRL survey was found at station 2 which was in a ship anchorage, whereas the station closest to the firefighting training area (11) was among the lowest concentrations found. Low naphthalene concentrations in all samples suggest that the PAH source is not likely to be from a fresh spill or groundwater intrusion of dilute unweathered product. Determining the mass of PAH in sediments at the Coaster's Harbor site would be difficult given the large amount of benthos covered by rock or confluent with eelgrass. PAH biodegradation rates were rapid given the low ambient concentrations suggesting that current surface water inputs of PAH would likely be metabolized in less than 100 days. The next sampling event will take place 30 October 2002 and will add measurements of the PAH concentration on particles in the upper water column that may be the primary source of PAH to the surface sediments.

Table 1. Total, low (LMW[1]) and high (HMW[2]) molecular weight PAH concentrations for the NRL survey (25-Jul-02) and the Tetratech (2-Jul-02) surveys of sediment from Coaster's Harbor and Narragansett Bay.

Date	Station				Total	LMW	HMW
	NRL	TT	Latitude (41° N)	Longitude (71° W)			
25-Jul-02	1	SD-JPC03	30.64744	21.7280	0.2	0.2	0.0
25-Jul-02	2	SD-423	30.85180	19.50881	3.2	1.6	1.5
25-Jul-02	3	SD-419	30.87775	19.57174	2.0	1.2	0.8
25-Jul-02	4	SD-421	30.87236	19.53866	0.3	0.2	0.1
25-Jul-02	5	SD-468	30.78719	19.4491	0.6	0.4	0.3
25-Jul-02	6	SD-467	30.89490	19.67683	0.1	0.0	0.1
25-Jul-02	7	SD-476	30.87485	19.74752	0.2	0.2	0.0
25-Jul-02	8	OFF-2	30.85039	19.76956	0.1	0.1	0.0
25-Jul-02	9	SD-412	30.86114	19.72027	0.1	0.1	0.0
25-Jul-02	10	SD-415	30.89734	19.64829	0.1	0.1	0.0
25-Jul-02	11	OFF-5	30.89048	19.60288	0.2	0.1	0.1
25-Jul-02	12	Landfill	32.54721	18.62169	0.3	0.3	0.0
25-Jul-02	13	Landfill	32.64068	18.66195	0.1	0.0	0.0
25-Jul-02	14	Creek	33.22345	18.41382	0.0	0.0	0.0
25-Jul-02	15	Boat launch	34.47007	17.31049	1.1	0.4	0.7
2-Jul-02		SD-410			2.5	0.8	1.7
2-Jul-02		SD-410			2.3	0.8	1.4
2-Jul-02		SD-410			0.8	0.3	0.5
2-Jul-02		SD-470			0.4	0.1	0.2
2-Jul-02		SD-471			10	3.3	6.9
2-Jul-02		SD-472			0.8	0.3	0.5
2-Jul-02		SD-473			1.3	0.5	0.8
2-Jul-02		SD-474			0.6	0.2	0.4
2-Jul-02		SD-474			0.7	0.2	0.5
2-Jul-02		SD-475			9.5	3.8	5.7
2-Jul-02		SD-476			0.8	0.3	0.5
2-Jul-02		SD-743			0.6	0.2	0.4
2-Jul-02		SD-JPC03			0.2	0.1	0.1

[1] Sum of Naphthalene, Acenaphthylene, Biphenyl, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene concentrations.
[2] Sum of Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[g,h,i]perylene concentrations.

Table 2. Individual PAH compounds measured by NRL and Tetratech during the July 2002 surveys. These include 2-methylnaphthalene (MNP), acenaphthene (ACE), carbazole (CAR), naphthalene (NAP), acenaphthylene (ACN), biphenyl (BIP), fluorene (FLE), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), pyrene (PYR), benzo[a]anthracene (BAA), chrysene (CHR), benzo[b]fluoranthene (BBF), benzo[k]fluoranthene (BKF), benzo[a]pyrene (BAP), indeno[1,2,3-cd]pyrene (IND), dibenz[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BGP).

Date	Station		MNP	ACE	CAR	NAP	ACN	BIP	FLE	PHE	ANT	FLU	PYR	BAA	CHR	BBF	BKF	BAP	IND	DBA	BGP
	NRL	TT																			
25-Jul-02	1	SD-JPC03				0.00	0.00	0.00	0.13	0.01	0.01	0.00	0.00								
25-Jul-02	2	SD-423					0.06	0.03	0.24	0.28	0.11	0.44	0.47	0.37	0.31	0.24	0.44	0.16			
25-Jul-02	3	SD-419					0.32	0.02	0.14	0.13	0.03	0.26	0.27	0.21	0.18	0.13	0.21	0.08			
25-Jul-02	4	SD-421					0.04	0.00	0.00	0.02	0.01	0.05	0.05	0.04	0.03	0.00	0.00	0.05			
25-Jul-02	5	SD-468					0.05	0.00	0.00	0.05	0.01	0.14	0.12	0.08	0.06	0.10	0.03				
25-Jul-02	6	SD-467								0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.04			
25-Jul-02	7	SD-476							0.09	0.02	0.01	0.04	0.03	0.02	0.02						
25-Jul-02	8	OFF-2								0.03	0.01	0.04	0.03	0.01	0.01	0.02					
25-Jul-02	9	SD-412								0.02	0.02	0.02									
25-Jul-02	10	SD-415					0.05	0.00	0.00	0.01	0.01	0.02	0.01	0.00	0.00						
25-Jul-02	11	OFF-5								0.03	0.01	0.04	0.04	0.02	0.02	0.00	0.06				
25-Jul-02	12	Landfill							0.13	0.04	0.01	0.06	0.04	0.01	0.00						
25-Jul-02	13	Landfill					0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.01			
25-Jul-02	14	Creek								0.00	0.00	0.00									
25-Jul-02	15	Boat launch				0.00	0.00	0.05	0.09	0.05	0.02	0.10	0.09	0.10	0.11	0.14	0.24	0.09			
2-Jul-02		SD-410	0.01	0.01	0.03	0.01	0.01		0.01	0.21	0.04	0.45	0.44	0.18	0.20	0.30	0.12	0.22	0.09	0.02	0.10
2-Jul-02		SD-410	0.01	0.02	0.03	0.01	0.01		0.02	0.28	0.06	0.41	0.40	0.16	0.17	0.25	0.10	0.20	0.07	0.02	0.08
2-Jul-02		SD-410	0.01	0.01	0.01	0.01	0.01		0.01	0.07	0.02	0.14	0.12	0.05	0.06	0.08	0.04	0.06	0.03	0.01	0.03
2-Jul-02		SD-470	0.01	0.01	0.01	0.01	0.01		0.01	0.03	0.01	0.06	0.05	0.02	0.03	0.04	0.02	0.03	0.01	0.01	0.02
2-Jul-02		SD-471	0.01	0.02	0.06	0.03	0.14		0.08	1.10	0.29	1.60	2.00	0.86	0.73	1.20	0.43	0.95	0.32	0.09	0.32
2-Jul-02		SD-472	0.01	0.01	0.01	0.01	0.01		0.01	0.07	0.02	0.12	0.13	0.05	0.06	0.10	0.04	0.07	0.03	0.01	0.03
2-Jul-02		SD-473	0.01	0.01	0.04	0.01	0.01		0.02	0.15	0.05	0.22	0.18	0.10	0.09	0.14	0.06	0.10	0.04	0.01	0.05
2-Jul-02		SD-474	0.01	0.01	0.01	0.01	0.01		0.01	0.07	0.01	0.11	0.11	0.04	0.05	0.06	0.03	0.05	0.02	0.01	0.03
2-Jul-02		SD-474	0.01	0.01	0.01	0.01	0.01		0.01	0.05	0.01	0.11	0.11	0.05	0.06	0.10	0.03	0.07	0.03	0.01	0.03
2-Jul-02		SD-475	0.01	0.10	0.13	0.01	0.04		0.15	1.40	0.50	1.50	1.70	0.72	0.62	0.89	0.33	0.77	0.28	0.09	0.30
2-Jul-02		SD-476	0.01	0.01	0.01	0.01	0.01		0.01	0.06	0.01	0.13	0.13	0.06	0.06	0.10	0.05	0.07	0.03	0.01	0.03
2-Jul-02		SD-743	0.01	0.01	0.01	0.01	0.01		0.01	0.05	0.01	0.10	0.09	0.04	0.04	0.07	0.03	0.05	0.02	0.01	0.02
2-Jul-02		SD-JPC03	0.01	0.01	0.01	0.01	0.01		0.01	0.01	0.01	0.04	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Table 3. Low, median, average, and high values for total PAH concentration in surface sediments for five aquatic ecosystems.

	Total PAH (ppm)					
Estuary	**Low**	**Median**	**Average**	**High**	**Samples**	**Sampling Events**
Narragansett Bay	0.1	0.4	1.4	10	28	2[3]
San Diego Bay	0.1	1.0	2.1	11	44	3
Charleston Harbor	0.0	3.5	6.6	58	187	12
Delaware & Schuylkill Rivers	0.4	15.2	16.8	89	169	5
Lower Chesapeake & Elizabeth River	0.0	6.4	35.6	636	58	6

[3] One sampling by NRL and one by Tetratech.

Table 4. Bacterial mineralization of sentinel PAHs to CO_2 was measured during the July 2002 survey.

Station	PAH Mineralization Rate (µg g^{-1} d^{-1})							
	Naphthalene		Phenanthrene		Fluoranthene		Catechol	
	AVG	SD	AVG	SD	AVG	SD	AVG	SD
1	1.28E-04	3.83E-05	0.00E+00		7.93E-04	8.22E-04	8.56E-03	4.07E-04
2	1.85E-03	4.22E-04	3.69E-04	2.19E-04	1.08E-03	1.53E-04	1.13E-02	2.78E-03
3	6.56E-04	1.15E-03	3.40E-04	3.24E-04	1.89E-03	1.17E-03	1.45E-02	9.44E-03
4	5.87E-04	2.17E-04	8.71E-05	2.43E-04	1.23E-04	9.53E-05	1.31E-02	2.72E-03
5	2.20E-03	5.59E-04	9.18E-04	2.17E-03	2.21E-03	7.48E-04	1.76E-02	1.51E-02
6	1.08E-03	8.96E-04	1.34E-04	3.87E-04	2.87E-03	1.98E-03	1.46E-02	1.90E-03
7	3.69E-04	1.06E-04	3.51E-05	2.29E-05	9.21E-04	7.59E-04	5.05E-03	1.73E-03
8	1.63E-03	3.98E-04	1.36E-04	7.82E-05	1.13E-03	1.13E-03	9.89E-03	7.23E-03
9	4.63E-04	2.72E-04	0.00E+00		1.04E-03	1.30E-03	4.68E-03	3.18E-03
10	1.89E-03	1.00E-03	1.62E-04	2.25E-04	0.00E+00		0.00E+00	
11	4.80E-03	9.56E-04	2.95E-04	2.26E-04	1.97E-03	1.39E-03	7.49E-03	6.56E-03
12	1.54E-03	3.34E-04	2.21E-04	2.17E-04	1.25E-03	1.65E-03	1.78E-02	6.71E-03
13	4.36E-04	4.13E-04	0.00E+00		1.61E-03	6.01E-04	2.75E-03	5.91E-03
14	2.31E-03	1.58E-04	5.86E-04	3.53E-04	0.00E+00		2.41E-02	8.80E-03
15	2.68E-03	1.28E-03	3.87E-04	1.14E-04	8.33E-04	1.75E-03	1.71E-02	3.70E-03

Table 5. PAH turnover time is a measure of the average time the compound would remain in the sediment sample pool given the no change in degradation rate.

Station	PAH Turnover Time (days)			
	Naphthalene	Phenanthrene	Fluoranthene	Catechol
1	ND[4]	ND	5	ND
2	ND	756	412	ND
3	ND	387	140	ND
4	ND	234	412	ND
5	ND	55	64	ND
6	ND	80	5	ND
7	ND	533	41	ND
8	ND	185	34	ND
9	ND	ND	21	ND
10	ND	61	ND	ND
11	ND	90	21	ND
12	ND	192	45	ND
13	ND	ND	6	ND
14	ND	5	ND	ND
15	ND	122	122	ND

[4] ND = Not Determined

Table 6. Bacterial production (leucine incorporation into bacterial proteins) was measured on sediment and water samples during the July 2002 survey of Narragansett Bay.

Station		Sample Type	Bacterial Production	
NRL	TT		AVG	SD
1	SD-JPC03	sediment	19.6	5.2
2	SD-423	sediment	12.9	2.0
3	SD-419	sediment	12.7	2.1
4	SD-421	sediment	4.9	0.4
5	SD-468	sediment	34.2	3.2
6	SD-467	sediment	17.3	0.5
7	SD-476	sediment	3.2	0.4
8	OFF-2	sediment	9.1	0.6
9	SD-412	sediment	4.1	0.2
10	SD-415	sediment	27.8	17.7
11	OFF-5	sediment	26.6	3.6
12	Landfill	sediment	14.6	4.5
13	Landfill	sediment	6.4	0.8
14	Creek	sediment	17.6	4.4
15	Boat launch	sediment	17.3	4.2
1	SD-JPC03	water	11.1	0.3
3	SD-419	water	11.1	2.0
6	SD-467	water	13.7	1.6
13	Landfill	water	8.1	0.7
14	Creek	water	12.9	1.0
15	Boat launch	water	12.5	3.7

Supporting References

Boyd, T. J., Montgomery, M. T., Spargo, B. J., Coffin, R. B., Steele, J. K., Pohlman, J. P., and D. Velinsky, " Characterization of intrinsic bioremediation within the Philadelphia Naval Complex Reserve Basin," NRL Technical Report, NRL/PU/6115--99-374, (1999)

Katz, C. N. 1998. Seawater polynuclear aromatic hydrocarbons and copper in San Diego Bay. TR 1768. Space and Naval Warfare Systems Center, San Diego, CA.

Kirchman, D. L. 1993. Leucine incorporation as a measure of biomass production by heterotrophic bacteria. pp. 509-512, In: Handbook of methods in aquatic microbial ecology. Kemp, P. F., Sherr, B. F., Sherr, E. B., and J. J. Cole (eds.) Lewis Publishers, Ann Arbor. 777 pp.

Kirchman, D. L., K'Nees, E., and R. Hodson. 1985. Leucine incorporation and its potential as a measure of protein synthesis by bacteria in natural aquatic systems. Appl. Environ. Microbiol. 49:599-607.

Montgomery, M. T., Boyd, T. J., Spargo, B. J., Coffin, R. B., Steele, J. K., Ward, D. M., and D. C. Smith. 1999. Bacterial assemblage adaptation in PAH-impacted ecosystems. In: *In Situ* and On-Site Bioremediation. B. C. Alleman and A. Leeson (eds.), Battelle Press, Columbus, OH, Vol. 5(8): 223-228.

Montgomery, M. T., Smith, D. C., Osburn, C. L., and T. J. Boyd. 2002. Bacterial degradation of aromatic hydrocarbons in surface sediments of temperate and tropical coastal ecosystems. *Eos, Transactions, American Geophysical Union*, Vol. 83, No. 4, OS21O-06.

Pohlman, J. W., Coffin, R. B., Mitchell, C. S., Montgomery, M. T., Spargo, B. J., Steele, J. K., and T. J. Boyd. 2002. Transport, deposition, and biodegradation of particle bound polycyclic aromatic hydrocarbons in a tidal basin of an industrial watershed. Environ. Monitor. Assess. 75: 155-167.

Smith, D. C., and F. Azam. 1992. A simple, economical method for measuring bacterial protein synthesis rates in seawater using ^{3}H-leucine. Mar. Microb. Food Webs 6(2):107-114.